PERGAMON

Applied Geochemistry 15 (2000) 1383–1397

Applied Geochemistry

www.elsevier.com/locate/apgeochem

Nature and practical implications of heterogeneities in the geochemistry of zinc-rich, alkaline mine waters in an underground F–Pb mine in the UK

Paul L. Younger*

Water Resource Systems Research Laboratory, Department of Civil Engineering, University of Newcastle, Newcastle Upon Tyne NE1 7RU, UK

Received 22 April 1999; accepted 12 January 2000
Editorial handling by R. Fuge

Abstract

Water pollution arising from base metal sulphide mines is problematic in many countries, yet the hydrogeology of the subsurface contaminant sources is rarely well-characterized. Drainage water pumped from an active F–Pb mine in northern England has unusual chemistry (alkaline with up to 40 mg.l^{-1} Zn) which profoundly impacts the ecology of the receiving watercourse. Detailed in-mine surveys of the quantity and quality of all ground water inflows to the mine were made. These revealed major, temporally persistent heterogeneities in ground water quality, with three broad types of water identified as being associated with distinct hydrostratigraphic units. Type I waters (associated with the Firestone Sill aquifer) are cool ($<10°$C), Ca–HCO$_3$–SO$_4$ waters, moderately mineralized (specific electrical conductance (SEC) $\leq$ 410 μS.cm^{-1}) with <4 mg.l^{-1} Zn. Type II waters (associated with the Great Limestone aquifer) are warmer ($\approx 15°$C), of Ca–SO$_4$ facies, highly mineralized (SEC $\leq$ 1500 μS.cm^{-1}) with ≤ 40 mg.l^{-1} Zn. Type III waters (in the deepest workings) are tepid ($>18°$C), of Ca–HCO$_3$–SO$_4$ facies, intermediately mineralized (SEC $\leq$ 900 μS.cm^{-1}) with ≤ 13 mg.l^{-1} Zn, and with significant Fe (≤ 12 mg.l^{-1}) and Pb (≤ 8 mg/l). Monotonic increases in temperature and Cl^{-} concentration with depth contrast with peaks in total mineralization, SO$_4$ and Zn at medium depth (in Type II waters). Sulphate, Pb and Zn are apparently sourced via oxidation of galena and sphalerite, which would release each metal in stoichiometric equality with SO$_4$. However, molal SO$_4$ concentrations typically exceed those of Pb and Zn by 2–3 orders of magnitude, which mineral equilibria suggest is due to precipitation of carbonate "sinks" for these metals. Contaminant loading budgets demonstrate that, although Type II waters amount to only 25% of the total ground water inflow to the mine, they account for almost 60% of the total Zn loading. This observation has important management implications for both the operational and post-abandonment phases of the mine life cycle.

1. Introduction

In many parts of the world, aqueous emissions of ecotoxic metals from mines are a major source of water pollution. The ecological problems arising from acidic mine drainage are widely appreciated (see Kelly,

---

* Fax: +44-191-222-6669.
E-mail address: p.l.younger@ncl.ac.uk (P.L. Younger).

PII: S0883-2927(00)00010-X

1988). Much of the ecological damage is caused by the smothering of the benthos by Fe hydroxide/oxyhydroxide deposits (generally termed "ochre" in the UK; Bowell and Bruce, 1995; Fuge et al., 1994), which can be so pervasive that they effectively preclude photosynthesis (e.g. Jarvis and Younger, 1997). It should be noted that the majority of mine water discharges which give rise to ochre precipitation are actually net-alkaline (e.g. NRA, 1994; Younger, 1998a), but are no less ecologically damaging for that (Jarvis and Younger, 1997). Ecotoxic metals other than Fe (e.g. Zn, Cu, Cd, Hg etc) are frequently encountered in the more acidic mine discharges (e.g. Banks et al., 1997; Fuge et al., 1994; Younger, 1998a), though it would be wrong to assume that such metals are restricted to net-acidic waters. The first objective of this paper is to document examples of net-alkaline mine waters of circum-neutral pH (and containing little Fe) which are nevertheless contaminated with up to 40 mg.l^{-1} of Zn.

The impacts of metalliferous mine water discharges on water resources and the ecological integrity of receiving watercourses have led regulatory agencies to impose rigorous aqueous emission standards on many mines. Where a mining operation is financially marginal, the costs of ensuring compliance with strict regulatory limits can be sufficiently onerous that they make continued mining uneconomic (Warhurst, 1999), conceivably resulting in outflows of contaminated water after the mine is flooded (Younger, 1997a; Younger and Harbourne, 1995). Avoidance of this calamity requires the development and application of cost-effective treatment methods for mine water effluents.

Mine water treatment can be achieved by a variety of means, which can be classed in two major categories (Hedin et al., 1994): active treatment and passive treatment. Active treatment of mine waters is most commonly achieved by means of alkali dosing and sedimentation (e.g. Bosman, 1983), though other (generally more costly) processes, ranging from bacterial sulphate reduction (Dvorak et al., 1992) through to reverse osmosis (Wilson and Brown, 1997), have all found applications to mine waters in appropriate circumstances. Passive treatment of mine waters is achieved by means of constructed wetlands and allied gravity-flow biogeochemical processes (Hedin et al., 1994; Younger, 1997b, 1998b).

Whether active or passive methods are used, it is commonly observed (see, for instance, Gray, 1999) that unit treatment processes tend to work most efficiently (in terms of percentage removal rates, etc) when they receive high influent concentrations. This phenomenon is well summarized in the aphorism concerning water treatment which holds that "it is easier to lower concentrations from 100 to 10 mg/l than from 10 to 1 mg/l". One corollary of this aphorism is that, if percentage efficiency were the only objective, it would be (somewhat paradoxically) better to treat a more concentrated effluent than a dilute one. In practical terms, this corollary only makes sense if one has the option of treating a high-concentration effluent of small volume in preference to a low-concentration effluent of large volume. In many wastewater treatment situations, there will be little scope for exercise of such a preference. However, where treatment of polluted groundwaters is concerned, there may well be scope for this, for polluted bodies of groundwater are well known to be markedly spatially heterogeneous, as a consequence of the myriad of dispersive and reactive processes which occur during pollutant transport (Fetter, 1999). Water entering deep mines is, of course, groundwater, and it is therefore reasonable to postulate that this will display heterogeneities in quality which could be exploited to optimize the cost-efficiency of effluent treatment.

The second objective of this paper is to demonstrate how careful geochemical characterization of heterogeneities in mine water quality within active workings can be used to identify the most highly contaminated components of the mine water yield. These highly contaminated components can then be isolated and subjected to separate, intensive treatment, leaving the bulk of (less contaminated) mine water to be discharged to the external environment with little or no treatment. The cost savings associated with this approach, compared to the traditional approach of treating the entire mine water yield, are considerable.

2. Methodology

The site chosen for the investigation was Frazer's Grove Mine, an underground fluorite/Pb mine in the North Pennine Orefield, UK (Fig. 1). Further details of the geological setting and mine layout are given in the following section. The work reported here formed part of a more substantial research programme which sought to assess and mitigate the environmental impacts of mine water discharges from Frazer's Grove Mine on the receiving watercourse. Details of the ecological, engineering and hydrological aspects of this project are reported elsewhere (Younger et al., 1995, 1998; Younger, 1998c).

Underground sampling sites were selected during reconnaissance visits in the Autumn of 1997, with weekly sampling for flows and hydrochemistry being undertaken in the period of January through April 1998. Fig. 2 illustrates schematically the layout of the mine and lettered sampling points.

The rigours of the underground working environment naturally make application of standard hydrological techniques (such as impeller flow metering) very difficult to implement. It was found that the most reliable results were obtained by measuring flows by a bucket-and-stopwatch approach. Where mine water emanated from (or could be temporarily diverted through) pipe ranges, this was readily accomplished. In come cases, corrections to data had to be made to allow for known periods of pump down-time. Where water cascaded through the mine roadways ceilings, tarpaulins were used to direct the water into a single jet, which was then amenable to bucket-and-stopwatch measurement.

Hydrochemical sampling was undertaken at the same points as flow measurements, and was supported by on-site analyses for alkalinity (using a hand-held digital titrator), pH, Eh (mV), temperature and conductivity (using portable electronic meters). The alkalinity titrations demanded a certain amount of practice to cope with the poor lighting. White backdrops lit by cap lamps of colleagues ensured that accurate, repeatable end-points were obtained. No problems were encountered with pH, Eh, temperature and conductivity measurements: re-measurement of calibration standards at the end of each sampling trip showed that the meters had not drifted in their performance by more than 2%. As in most other studies the absolute value of the Eh measurements is nevertheless suspect, except for waters such as the 295W Exploration Borehole, the Rake Level and Greencleugh, in which sufficient Fe is present for the Fe^{2+}/Fe^{3+} couple to dominate the overall redox response. Samples were collected in new 500 ml plastic bottles, with the cation samples being preserved at the time of collection by addition of 3 drops of concentrated HNO_3. On-site filtration was usually impractical during underground visits, due to restrictions of time (arising from the need to synchronize activities with mine production cycles). On the few occasions when there was time for on-site filtration before filling of bottles, comparisons of filtered and unfiltered waters revealed only minor differences. Greatest uncertainties in relation to non-filtered samples arise for the two stations on 260 and 270 levels, where the water was often turbid due to concurrent mining activities. Comments on these uncertainties are given in Section 4.

At ground surface, flow measurements and sampling were also undertaken at the mouths of mine adits where water emerges by gravity flow, and at the top of the No 1 shaft (Fig. 2) where the entire underground water make (i.e. the total amount of water entering the

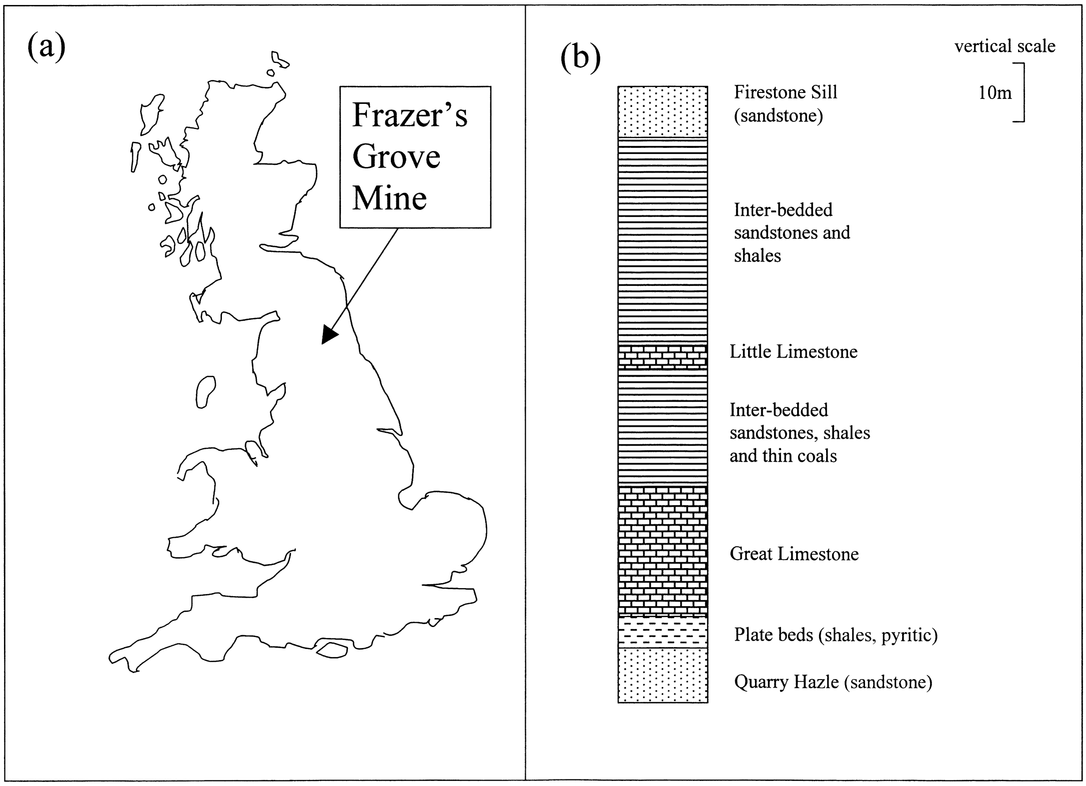

Fig. 1. (a) Location of Frazer's Grove Mine within the UK (b) Simplifed geological succession for the study area, showing the relative positions of stratigraphic units mentioned in the text.

workings) is brought to the surface by means of a submersible pump. The very substantial flow from this pump was determined by logging pump run times and making occasional checks of instantaneous flow rate by a "bin-and-stopwatch" method.

After filtering all samples in the laboratory to 0.45 μm, analyses were undertaken in accordance with the Standard Methods of the American Public Health Association. Cations were determined by atomic absorption spectrophotometry and inductively coupled plasma optical emission spectroscopy, and anions by ion chromatography. The dilutions necessary to allow passage of waters with such high concentrations of SO_4 through the chromatograph column result in a loss of accuracy for some anions (such as F^-) which are present at low concentrations. The values obtained for F have been excluded from Table 1 for this reason. The O and H isotopes were analysed at the British Geological Survey's Wallingford laboratory, using dedicated preparation lines and dipole mass spectrometers in accordance with well-established procedures (G Darling, BGS, personal communication 1996).

Speciation of the waters was modeled, and calculation of mineral saturation indices performed, using the well-known US Geological Survey code WATEQ4F (Ball and Nordstrom, 1991). WATEQ4F is particularly suited to the modeling of mine waters as the database compiled by Ball and Nordstrom (1991) draws upon several decades of research into mine water geochemistry. Recent examples of the application of WATEQ4F to mine waters are presented by Younger (1995, 1998a) and Chen et al. (1997). All of the analytes reported in Table 1 were used in the WATEQ4F runs. Although F was excluded from Table 1 because of analytical errors arising from the dilutions necessary for the ion chromatograph, and was therefore excluded from the WATEQ4F analyses, the fact that it occurs at low concentrations in these waters (typically less than 1 mg.l^{-1}, reflecting the low solubility of CaF_2 at the ambient temperatures and pressures) precludes it having a dominating influence on speciation.

3. Frazer's Grove Mine

"Frazer's Grove Mine" is the collective name for four adjoining series of underground workings (all operated by the same company) in the Rookhope val-

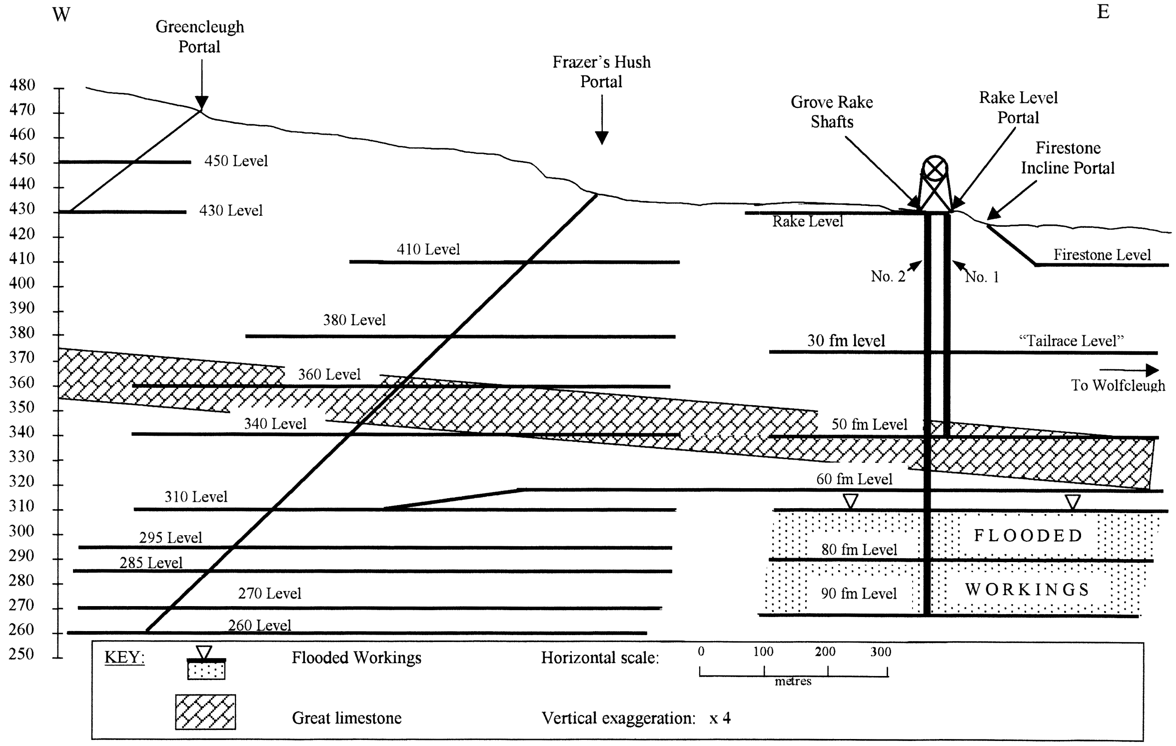

Fig. 2. Simplified cross-section (parallel to the strike of the Greencleugh Vein) through workings of Frazer's Grove F–Pb mine, showing named localities where water quality samples were collected.

Table 1
Mean hydrochemical results for sites in Frazer's Grove mine shown on Fig. 2. All values mg.l^{-1} except where indicated. SEC = specific electrical conductance; (Alk is alkalinity in mg.l^{-1} as $CaCO_3$ equivalent)

Location	Type	pH	SEC (μS/cm)	Temp °C	Eh (V)	Fe	Cu	Pb	Zn	Ca	Mg	Na	K	SO_4	Cl	Alk (as $CaCO_3$)	δ^2H	$\delta^{18}O$
Rake level	I	7.4	260	8.1	−0.016	1.4	0.01	0.18	0.8	29	8.2	14	4	60	21	45		
Greencleugh	I	6.7	410	7.9	0.025	0.8	0.01	0.18	2	85	15.7	8	7	126	18	123	−51	−8.6
Firestone incline	I	7.4	360	9.7	0.01	3	0.04	0.001	3.5	112	14	7	6	162	23	137		
295W Exp BH	I	6.7	290	9.7	0.021	5	0.56	0.23	0.7	48	8.5	7	5	73	16	88		
285E Total make	II	7.2	1280	15.3	−0.008	0.3	0.06	0.02	19	270	60	21	20	870	24	120	−52	−8.3
285E Hopper	II	7	1020	13.9	−0.002	0.6	0.04	0.03	27	205	42	11	15	695	31	63		
285E In-bye water	II	7.2	1350	15.1	−0.007	4	0.05	0.02	10	264	71	18	23	960	24	102		
310 Local make	II	7	1510	14.8	0.005	3	0.02	0.53	21	313	86	19	19	1080	42	92	−53	−8.3
270 Fan rise	III	7.4	950	18.5	−0.018	7	0.02	3.83	14	182	30	67	26	528	30	140		
260 Sump	III	7.7	820	18.5	−0.036	11	0.04	5.6	0.4	127	15	83	26	260	42	185		
Sun vein sump	I	7.1	940	17.4	−0.002	0.3	0.05	0.01	8	142	23	53	25	350	16	266	−52	−8.3
No 1 shaft	III	6.8	890	12.6	0.017	3.5	0.55	0.95	13	155	35	17	13	535	17	56		

ley, Weardale, County Durham, UK (Figs. 1 and 2). The workings are developed in a series of sub-vertical hydrothermal veins which form part of the extensive North Pennine Orefield (Dunham, 1990). This orefield has a history of mining dating back many centuries, and it was for much of its life the world's leading source of Pb. It has also been a major producer of Zn, Ba and F, the latter in the form of fluorite. The veins in which the economic deposits occur cut fairly flat-lying sedimentary rocks (Fig. 1(b); principally shales, sandstones and limestones) of Lower Carboniferous age. The most prominent formation in the Frazer's Grove district is the Great Limestone (Figs. 1(b) and 2), which maintains a thickness in excess of 20 m throughout most of the orefield. The veins pinch as they pass through soft, shaley strata, but swell to several metres width where they cut competent sandstones and limestones. The most productive sections of the majority of veins have been encountered where the veins cut the Great Limestone.

Frazer's Grove Mine is developed in three intersecting veins, all of which carried substantial quantities of fluorite (CaF_2), with subsidiary siderite ($FeCO_3$) and quartz (SiO_2). Economically important metal sulphide minerals occur rather sparsely in these veins. Inspection of vein material currently worked in Frazer's Grove reveals the most abundant sulphide mineral to be galena (PbS), which is present in large euhedral crystals (individuals being up to 3 cm diameter) and polycrystalline masses (up to 30 cm diameter). Chalcopyrite ($FeCuS_2$) occurs as thin dendritic wafers between siderite and fluorite masses near the footwall of the vein. Pyrite is very rare, though it sometimes occurs as minor, medium-grained inclusions within large masses of galena. These inclusions oxidise following exposure, giving rise to "rusty rims" around galena crystals where these adjoin fluorite or quartz. Sphalerite is generally fine grained, but locally abundant to judge from analyses of ore concentrates.

Brief details of the mining history and modern dewatering arrangements in each of the four mining operations at Frazer's Grove (Fig. 2) are as follows:

3.1. Grove Rake Mine

This is the body of workings accessed by the two shafts (Fig. 2), which worked the Grove Rake and Red veins for Pb between 1815 and 1916 (Dunham, 1990), and subsequently for fluorite until the 1970s. These workings are connected to the more recent Frazer's Hush workings to the west by only one roadway (the 60 fathom level; Fig. 2). This roadway is used to complete the ventilation circuit, provide secondary egress from the mine and to route pumped drainage from Frazer's Hush to the sump in the No 2 shaft, where it mixes with Grove Rake waters before being pumped to the surface for disposal.

3.2. Rake level/Firestone Incline workings

Although always administered as part of Grove Rake Mine, these workings are not accessible via the Grove Rake shafts, and were always worked via the two drift-type drivages into the hillside from which they draw their names (Fig. 2). Minor dewatering operations within these workings deal with local water inflows by pumping to both portals.

3.3. Frazer's Hush Mine

This is the main area of recent and current working, and exploits the Greencleugh Vein. The mine is accessed by the "1-in-4 Dib" (i.e. inclined roadway) some 600 m west of the Grove Rake shafts (Fig. 2). Water enters the Frazer's Hush workings at a number of horizons, but most prolifically at and below the 310 level (Fig. 2).

3.4. Greencleugh Mine

Greencleugh Mine worked higher portions of the Greencleugh Vein, principally in the Great Limestone and overlying strata, a little to the west of those areas worked from Frazer's Hush 1-in-4 Dib. This mine was worked intermittently until December 1995, since which time pumping of the mine sump (discharged via the portal) has been maintained to avoid dangerous accumulations of water above active workings in Frazer's Hush.

4. Results

4.1. Flow measurements

Before this investigation, there was little accurate information on the quantities of water pumped from the Frazer's Grove complex. (This state of affairs is not uncommon in mining operations worldwide.) Although pump run times were recorded as part of safety procedures, instantaneous flow measurements on individual inflows were never made, and estimates of the total water yield of the mine were based upon the pump manufacturers specification data. Development of a detailed water budget for the mine on the basis of the new underground flow measurements was therefore a priority. A summary of the mine water budget is given

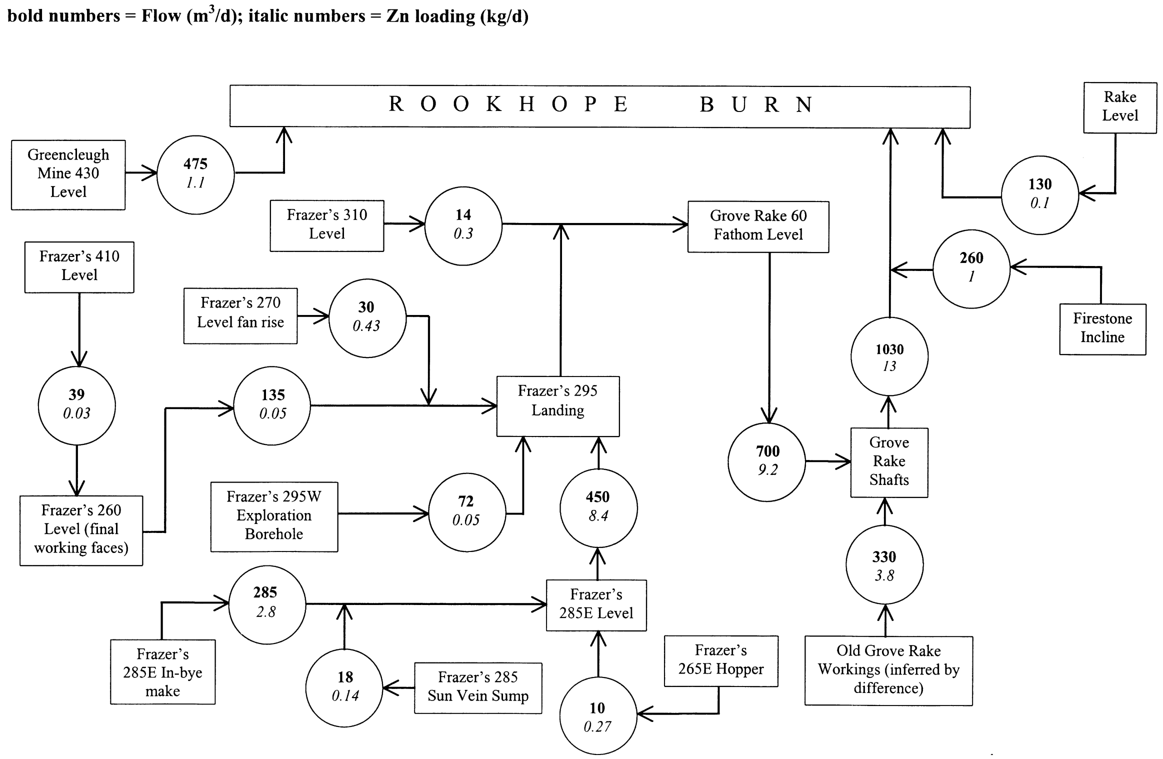

Fig. 3. Flow chart summarizing the mean water and Zn-loading budget for Frazer's Grove Mine.

Table 2
Mean results of speciation of Zn (calculated using WATEQ4F) for the Frazer's Grove Mine waters listed in Table 1. Values are the percentage of total Zn activity

Location	"Type"	Zn^{2+}	$ZnCl^+$	$ZnCO_3$	$Zn(CO_3)_2^{2-}$	$ZnHCO_3^+$	$ZnOH^+$	$Zn(OH)_2$	ZnOHCl	$ZnSO_4$	$Zn(SO_4)_2^{2-}$
Rake level	I	82.94	0.05	5.5	0.07	4.81	0.48	0.5	0.03	5.6	0.03
Greencleugh	I	78.05	0.03	2.44	0.02	11.06	0.08	0.02	0	8.21	0.08
Firestone incline	I	67.98	0.04	11.84	0.5	10.24	0.41	0.36	0.02	8.51	0.11
295W Exp BH	I	82.5	0.04	2.13	0.01	8.98	0.11	0.02	0	6.18	0.04
285E Total make	II	61.52	0.04	5.05	0.16	6.3	0.31	0.1	0.01	25.05	1.48
285E Hopper	II	67.51	0.05	1.9	0.02	3.84	0.2	0.05	0.01	25.17	1.24
285E In-bye water	II	61.15	0.04	4.23	0.11	5.33	0.3	0.1	0.01	26.97	1.77
310 Local make	II	62.56	0.06	2.32	0.04	4.71	0.19	0.04	0.01	28.05	2.01
270 Fan rise	III	60.68	0.06	10.7	0.62	7.63	0.66	0.27	0.02	18.67	0.68
260 Sump	III	49.8	0.07	25.82	3.81	9.05	1.15	0.97	0.05	9.11	0.17
Sun vein sump	III	58.67	0.03	10.81	0.59	15.58	0.31	0.07	0.01	13.58	0.34
No 1 shaft	III	70.8	0.03	1.18	0.01	3.87	0.12	0.02	0	23.05	0.92

in Fig. 3, from which it is clear that the Frazer's Hush workings are the most prolific source of water, yielding around 700 $m^3.d^{-1}$.

4.2. Mine water chemistry

Mean hydrochemical results for all mine water discharges at Frazer's Grove, and subsidiary points within the Frazer's Hush workings, are given in Table 1. It is immediately apparent that the most problematic component of these waters is Zn, which is present at mean concentrations ranging up to 27 $mg.l^{-1}$ (in the 285E Hopper locality). (Individual samples at the same point yielded concentrations as high as 40 $mg.l^{-1}$). Elevated concentrations of Pb are also apparent in some analyses, particularly those of 260 level, 270 level and No 1 shaft. However, as these three locations generally yielded turbid water due to active mineral extraction, and given that galena was present in large quantities in the vein at the time of the site visits, it is possible that the elevated Pb concentrations are the result of sample contamination by galena particles suspended in these waters at the time of sampling and preservation with acid. In any case, Pb concentrations are typically 1–2 orders of magnitude lower than those of Zn. Copper is often detected (as expected from the presence of chalcopyrite in the vein), but is typically 3 orders of magnitude lower in concentration than Zn.

By combining the Zn concentrations with the synchronously measured flows, it has been possible to calculate a detailed Zn loading budget for the mine (Fig. 3). The significance of this budget is discussed in the following section.

4.3. Speciation and mineral saturation index modeling

WATEQ4F was run for all available analyses, using the Debye-Hückel formulation to speciate the waters. While the code predicts the distribution of aqueous species for all analytes entered in the input files, space (and lack of novelty) precludes the presentation of most of the results here. However, given the applied interest in the behaviour of Zn as a contaminant at this site, the speciation of that metal is summarized in some detail in Table 2.

WATEQ4F calculates the saturation index (SI), which is defined as $\log(IAP/K_t)$, where IAP is the ion activity product and K_t the solubility product (tabulated in the WATEQ4F database for a wide variety of mineral phases; Ball and Nordstrom, 1991). In practice, very few minerals will satisfy one or more of the following criteria:

- contain species (such as ecotoxic metals) which are of interest for study purposes in the relevant waters;

- be visibly present in the local strata, or;
- be sufficiently close to saturation (i.e. with an SI value close to zero) that they could feasibly be influencing the dissolved concentrations of species of interest.

For this particular problem, minerals which satisfy these criteria are calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), siderite ($FeCO_3$), smithsonite ($ZnCO_3$), amorphous hydrated Zn carbonate ($ZnCO_3.1H_2O$), gypsum ($CaSO_4.2H_2O$) and cerussite ($PbCO_3$). The modelled SI values for these minerals in relation to mean water quality at various measuring points within the mine system are presented in Table 3.

Two further minerals might be postulated as possible sinks for Zn in this system. The first of these is goslarite ($ZnSO_4.7H_2O$), the formation of which might be anticipated in waters so rich in Zn and SO_4. However, in no case was the SI value obtained for goslarite greater than −4. The second (and more plausible) possible solid phase sink for Zn is hydrozincite ($ZnCO_3.3Zn(OH)_2$; Dunham, 1990), which has actually been observed actively precipitating in abandoned mines further west in the orefield (Nuttall and Younger, 1999). However, thermodynamic data for this mineral are not yet sufficiently well established to allow its inclusion in the WATEQ4F database. If (as seems likely) the precipitation of hydrozincite actually occurs via an amorphous hydrated Zn CO_3 predecessor, then the presence of that mineral in the current database will suffice for predicting by proxy the likelihood of precipitation of hydrozincite (though not its dissolution).

Problems with direct measurement of Eh (which are commonly encountered in studies such as this) were noted above. To assess the degree to which the uncertainties in measured Eh values propagate errors into the speciation modelling, simple sensitivity analyses were undertaken. These involved changing the Eh in all of the analyses in the WATEQ4F input file between reasonable limits (−100 to +100 mV), and evaluating the changes in speciation of Fe, Zn and Cu, and in the SI values for the minerals listed in Table 3. Although minor changes in speciation were observed, in no case did these result in any of the studied minerals shifting from sub-saturation to super-saturation or vice versa. This may be because of the narrow range of possible species for these metals in such hard waters at neutral pH. It was therefore concluded that the uncertainties in Eh measurement were not greatly damaging the interpretation of the WATEQ4F output.

5. Discussion

5.1. Nature of the Frazer's Grove Mine waters

In terms of overall physico-chemical characteristics (Table 1), it is possible to distinguish three volumetrically-important types of water in the Frazer's Grove workings. The three types plot in distinct fields on a standard Piper diagram (Fig. 4). The overall properties of the three water types are as follows:

5.1.1. Type I

Cool (temperature <10°C), moderately mineralised (conductivity ≤410 μS/cm), soft to moderately hard waters of Ca–HCO_3–SO_4 facies (Fig. 4), with relatively low concentrations of Zn (≤4 mg/l). These waters are typical of the Rake Level, the Firestone Incline, Greencleugh, Frazer's 410 level, and the 295W exploration borehole (Table 1), all of which represent drainage

Table 3
Mean saturation indices ($\log(IAP/K_T)$ values) for the waters listed in Table 1, in terms of selected minerals known or inferred to be present in the sequence mined at Frazer's Grove, calculated using WATEQ4F

Location	Type	Calcite	Dolomite	Siderite	Smithsonite	$ZnCO_3.1H_2O$	Gypsum	Cerrusite
Rake level	I	−1.238	−2.937	−0.339	−1.664	−1.212	−2.048	−0.084
Greencleugh	I	−1.11	−2.869	−0.942	−1.621	−1.166	−1.4	−0.217
Firestone incline	I	−0.245	−1.272	0.035	−0.67	−0.237	−1.222	−2.304
295W Exp BH	I	−1.427	−3.488	−0.201	−2.115	−1.682	−1.797	−0.146
285E Total make	II	−0.244	−0.925	−0.961	−0.238	0.13	−0.432	−1.153
285E Hopper	II	−0.825	−2.142	−1.111	−0.526	−0.142	−0.574	−1.115
285E In-bye water	II	−0.337	−1.03	0.087	−0.595	−0.225	−0.415	−1.173
310 Local make	II	−0.535	−1.42	−0.307	−0.536	−0.163	−0.333	0.155
270 Fan rise	III	−0.045	−0.612	0.768	−0.009	0.322	−0.715	1.161
260 Sump	III	0.3	−0.066	1.033	−1.171	−0.84	−1.064	1.365
Sun vein sump	III	−0.122	−0.789	−0.605	−0.26	0.083	−0.925	−1.418
No 1 shaft	III	−1.166	−2.804	−0.568	−1.065	−0.666	−0.736	0.294

from the workings in the Firestone Sill sandstone. The speciation of Zn in Type I waters (Table 2) is dominated by free Zn^{2+} at around 80% of the total, with the two carbonate species $ZnCO_3^0$ and $ZnHCO_3^+$ accounting for most of the remainder. $ZnSO_4^0$ accounts for only 5.5–8.5% of the total Zn (which, as will be seen, is in stark contrast to its importance in the Type II waters). With the exception of the Firestone Incline water, which appears to be saturated with respect to siderite, the Type I waters are undersaturated with respect to all minerals listed in Table 3 (although cerussite is very close to saturation in the Rake Level and 295W exploration borehole waters). The lack of saturation with respect to common carbonates is consistent with the shallow provenance of the Type I waters, and the fact that they are sourced from a ferruginous sandstone (the Firestone Sill) which is not overlain by carbonates. Type I waters account for around 50% of the total Frazer's Grove water make, but only 15% of the total Zn loading (Fig. 3).

5.1.2. Type II

Warmer (temperature $\leq 15°C$), highly mineralised (conductivity ≤ 1500 μS/cm), hard to very hard waters of $Ca–SO_4$ facies (Fig. 4), with high concentrations of Zn (≤ 30 mg/l). Type II waters are encountered on the 310 and 285E levels of the Frazer's Hush workings, and are associated with drainage through abandoned workings which underdrain the Great Limestone horizon. The speciation of Zn in the Type II waters is quite different from that seen in Type I, in that the CO_3 species ($ZnCO_3^0$ and $ZnHCO_3^+$) are relatively unimportant (totalling only 6–11% on average), while the SO_4 species $ZnSO_4^0$ (and to a lesser extent $Zn(SO_4)_2^{2-}$) account for 26–30% of the total, leaving little more than 60% as the free ion Zn^{2+}. Type II waters are much closer to saturation with respect to the common carbonate minerals (calcite, dolomite and siderite) than are the Type I waters, but still do not reach saturation (except in the case of siderite in the 285E In-Bye water). However, the 285E total make is saturated with respect to amorphous hydrated Zn CO_3 (Table 3), and the 310 local make is very close to saturation with this phase also. This suggests that precipitation of hydrated Zn CO_3 (or, indeed, hydrozincite, as discussed in the preceding section) may be imposing an upper limit on dissolved Zn concentrations in these waters. There is no such mineral control active for SO_4, however, since gypsum remains significantly under-saturated (even though it is closer to saturation in these waters than in Types I or III). It is interesting also to note that cerussite is markedly under-saturated in these waters, which suggests that galena oxidation has virtually ceased in the disused workings through which the Type II waters drain. This is in contrast to the situation in the active workings (as discussed below). Type II waters account for around 25% of the total Frazer's Grove water make, but 57% of the total Zn loading (Fig. 3).

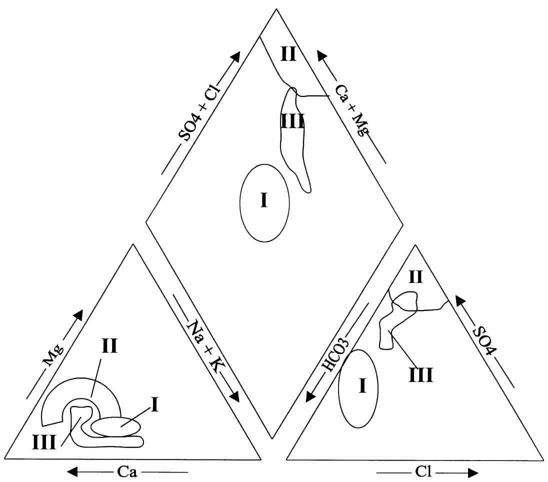

Fig. 4. Piper diagram illustrating the proportions of major ions in the Type I–III waters in Frazer's Grove Mine.

5.1.3. Type III

Tepid (temperature $>18°C$), fairly highly mineralised (conductivity around 900 μS/cm), hard waters of $Ca–SO_4$ facies with significant HCO_3 (Fig. 4), with elevated Fe (≤ 12 mg/l), Zn (≤ 14 mg/l) and Pb (≤ 8 mg/l). These waters are associated with active workings (260 and 270 level waters) in the Quarry Hazle sandstone and the underlying "grey beds" of siltstone and mudstone, in which vein mineral sources of Fe, Zn and Pb (ie siderite, sphalerite and galena respectively) were being drilled and blasted daily at the time of sampling. Type III waters closely resemble the mixed water pumped from the Grove Rake shafts, with the exception that the latter does not contain appreciable Pb (<1 mg/l). The speciation of Zn in Type III waters results in the lowest proportion of free Zn^{2+} (at 60% or less) seen in any of the three types. The proportions of Zn complexed with CO_3 and SO_4 are roughly equal. Hence the speciation of these waters in some senses resembles a compromise between the distinct speciations seen in the Type I and II waters. In terms of mineral saturation indices (Table 3), the Type II waters are saturated (or very nearly so) with respect to calcite (except in the case of the No 1 shaft water), and even with respect to dolomite in the case of the 260 sump waters. The 260 and 270 waters are saturated with respect to siderite, which is consistent with the observed abundance of siderite in the Greencleugh Vein on these levels. The 270 waters are also saturated with respect to smithsonite and amorphous hydrated Zn CO_3. With the exception of the Sun Vein sump waters (which drain inactive workings), the Type III waters all display super-saturation with respect to cerussite, strongly suggesting that the limited concentrations of dissolved Pb in the waters can be attributed to precipitation of this mineral. In this connection, it is interesting to note the following comments of Dunham (1990) in relation to mines a little further west in the orefield: "Cerussite and anglesite are the common alteration-products of galena, forming a white coating to the grains and masses of the mineral, sufficient in many instances to protect it from further alteration". Although anglesite is strongly undersaturated in these waters (with SI in the range −0.9 to −1.5) it seems likely that precipitation of cerussite could explain why Pb is far less mobile than Zn in waters draining Frazer's Grove and other mines (e.g. Nuttall and Younger, 1999), even though galena is far more abundant than sphalerite in the ore bodies. If, as Dunham (1990) suggests, cerussite precipitates gradually develop so far as to "seal" galena surfaces, then it is also possible to understand why Pb concentrations are so much lower in waters draining the disused workings (producing Type II waters) than in these Type III waters. Presumably, sphalerite surfaces do not become so heavily sealed by Zn CO_3 precipitates, hence facilitating the sustained release of Zn into Type II waters. Type III waters account for around 25% of the total Frazer's Grove water make, and 28% of the total Zn loading (Fig. 3).

A fourth type of water does not appear in the active workings, and hence is not listed in Table 1. Indeed it has been observed only once during the life of the mine, during a temporary pump failure at the Grove Rake shafts in late March/early April 1996. When the pumps are operating normally in this part of the mine, the water level is maintained at around 312 m AOD (i.e. above Ordnance Datum, the UK sea level datum). By the time pumping recommenced, the water level had risen to around 328 m AOD, flooding some previously dry strata between the Quarry Hazle and the Great Limestone (Fig. 1). The so-called "plate beds" (i.e. shales) in this sequence of strata are pyritic (uniquely amongst the shales seen in the Frazer's Grove workings). Subsequent inspection of these strata underground reveals them to carry a heavy mantle of white and yellow acid generating salts (*sensu* Bayless and Olyphant, 1993). Rapid dissolution of these salts during the flooding incident explains the atypically acidic nature of the mine water subsequently pumped from the Grove Rake shafts, which had the following characteristics when sampled on 4 April 1996: pH 3.56; SO_4 902 mg.l^{-1}; total Zn 26.6 mg.l^{-1}; total Fe 20.1 mg.l^{-1}; total Mn 22 mg.l^{-1}; total Al 14.6 mg.l^{-1}. Sustained pumping was accompanied by a rapid return to water of Type III, which persisted thereafter.

With the exception of these acidic waters associated with transient flooding of low-permeability strata, the Frazer's Grove mine waters are all strongly net-alkaline (Table 1). As noted above, the resolution of the waters into three types is explicable in terms of the stratigraphic horizons with which they are associated. As the strata in this area are only gently dipping (Fig. 2), one would expect the distinct plotting positions of the three types on Fig. 4 to be reflected in some differentiation in key solutes over depth in the workings. Fig. 5(a) shows the generally monotonic increase in mine water temperature and Cl^- content with increasing depth. These patterns suggest (as would be anticipated) an increasing proportion of long-residence time (and therefore warmer and more saline) groundwater entering the mine as depth increases. Nevertheless, by comparison with previously published values for meteoric water and mine waters in the adjoining Durham Coalfield (Sheppard and Langley, 1984), the δ^2H and $\delta^{18}O$ values found throughout this mine are consistent with the inference that all of the waters are of relatively modern meteoric origin. It therefore follows that the elevated temperatures of these waters are not due to upwelling of ancient, warm waters from depth, but rather that they reflect warming of inflowing shallow groundwaters in response to the unusually high geothermal gradient associated with the underlying Weardale Granite (which has been extensively investigated by Dunham (1990) by means of the nearby Rookhope Borehole).

Fig. 5(b) shows the profiles of conductivity and SO_4

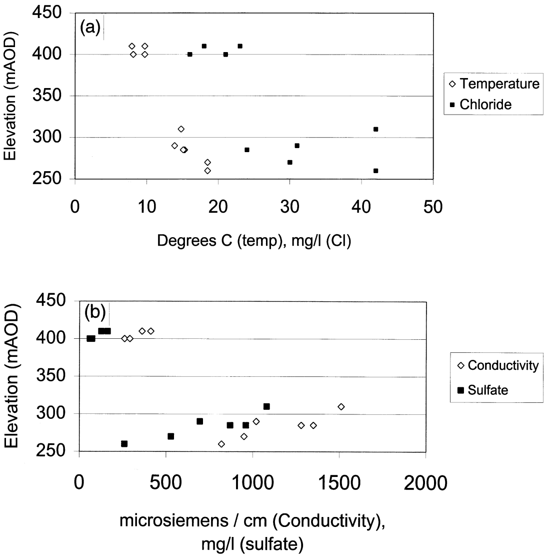

Fig. 5. (a) Temperature and Cl^- as a function of elevation within the Frazer's Grove Mine workings. (b) SO_4 and conductivity as a function of elevation within the Frazer's Grove Mine workings.

with elevation. This indicates that the most heavily mineralized waters are not associated with the deepest workings, but rather with the workings between 310 and 285 mAOD, into which water flows from the (immediately overlying) Great Limestone via old workings in the Greencleugh Vein. These field relations strongly suggest that the very high SO_4 concentrations typical of the waters at these depths (which are all Type II waters) are not features of unaltered deep groundwaters, but rather are associated with dissolution of sulphide minerals in and around the Greencleugh Vein.

In order of decreasing abundance, the sulphide minerals present in the Greencleugh Vein are galena, chalcopyrite, sphalerite and pyrite. Sphalerite is unique amongst the four in that it occurs as very fine-grained crystals, which would be expected to be far more reactive than the medium- and large-grained euhedra of galena, chalcopyrite and pyrite. In the discussion of the three water types above, it was noted above that mobile Pb is only found in the Type III waters, which are associated with areas of active extraction. Type II waters, which drain from disused workings which have been inactive since the early 1990s, generally have very low concentrations of Pb, though amongst the highest concentrations of Zn. This suggests that galena dissolution is not very vigorous save where the large euhedra are being finely sub-divided by the mining process. It is also feasible, as discussed above, that coatings of cerussite on galena crystals in the inactive workings limit further dissolution (cf Dunham, 1990).

High SO_4 concentrations are typical of pyrite oxidation waters, and are therefore often expected to be accompanied by a low pH. However, where there is little pyrite to be oxidized, then oxidation of the other sulphide minerals present in this orebody would not be expected to give rise to acidic pH values. For instance, oxidation of sphalerite can be simply written:

$$\mathrm{ZnS} + 2\mathrm{O}_{2(\mathrm{aq})} \rightarrow \mathrm{Zn}^{2+}_{(\mathrm{aq})} + \mathrm{SO}^{2-}_{4(\mathrm{aq})} \tag{1}$$

And similarly for galena:

$$\mathrm{PbS} + 2\mathrm{O}_{2(\mathrm{aq})} \rightarrow \mathrm{Pb}^{2+}_{(\mathrm{aq})} + \mathrm{SO}^{2-}_{4(\mathrm{aq})} \tag{2}$$

and chalcopyrite:

$$\mathrm{CuFeS}_2 + 4\mathrm{O}_{2(\mathrm{aq})} \rightarrow \mathrm{Cu}^{2+}_{(\mathrm{aq})} + \mathrm{Fe}^{2+} + 2\mathrm{SO}^{2-}_{4(\mathrm{aq})} \tag{3}$$

None of these oxidation reactions directly yield protons on the right-hand side. However, the Fe^{2+} yielded by oxidation of chalcopyrite (3) may be hydrolysed to form ochre:

$$\mathrm{Fe}^{3+} + \mathrm{H}_2\mathrm{O} \rightarrow \mathrm{Fe(OH)}_3 + 3\mathrm{H}^+ \tag{4}$$

which generates acidity. Alternatively, Fe^{3+} may be consumed in the oxidation of (for instance) sphalerite, according to (Boon et al., 1998):

$$\mathrm{ZnS} + 2\mathrm{Fe}^{3+}_{(\mathrm{aq})} \rightarrow \mathrm{Zn}^{2+}_{(\mathrm{aq})} + 2\mathrm{Fe}^{2+} + \mathrm{S}^0_{(\mathrm{aq})} \tag{5}$$

Whence the elemental S (S^0) is subsequently oxidized to SO_4^{2-}:

$$\mathrm{S}^0 + 1.5\mathrm{O}_2 + \mathrm{H}_2\mathrm{O} \rightarrow \mathrm{SO}_4^{2-} + 2\mathrm{H}^+ \tag{6}$$

(Similar equations to Eqs. (5) and (6) can be written for the oxidation of chalcopyrite and galena).

By either mechanism of Fe transformation (i.e. Eq. (4) or (6)), it is clear that chalcopyrite oxidation can ultimately yield acidity, even though the first step in the reaction chain, Eq. (3), is not acid-generating. Consequently if more chalcopyrite than sphalerite were oxidizing in this environment, we would expect to see rather more dissolved Fe and Cu, and a somewhat lower pH, than are in fact encountered (Table 1). If chalcopyrite oxidation is thus volumetrically unimportant, and (as postulated above) cerussite "sealing" of crystal surfaces limits the sustained oxidation of galena, then the bulk of SO_4 in the Frazer's Grove waters must be sourced from sphalerite oxidation. In that case, it is possible to assess the amount of attenuation of Zn which is occurring within the mined strata by means of simple mass-balance calculations.

Table 4 lists mean molar ratios of S:Zn for all the principal sampling points at Frazer's Grove. SO_4 can be expected to have been transported conservatively from the sites of sphalerite oxidation, as the only feasible mineral sinks for SO_4 (gypsum and goslarite) are always undersaturated in Frazer's Grove mine waters (Table 3), and the measured Eh values (Table 1) are too high (and C sources probably too scarce) for SO_4 reduction to be a volumetrically important process. If

Table 4
Mean molar ratios of total S to total Zn in the Frazer's Grove Mine waters

Location	Molar ratio of S to Zn
Rake level	51
Greencleugh	43
Firestone incline	31
295W Exp BH	71
285E Total make	31
285E Hopper	17.5
285E In-bye water	65
310 Local make	35
270 Fan rise	26
260 Sump	442
Sun vein sump	30
No 1 Shaft	28

Zn were also transported conservatively from sphalerite oxidation sites, then in view of the stoichiometry of the mineral (ZnS), one would expect the S:Zn molar ratio to be unity. It is immediately apparent from Table 4 that there are no values of this ratio even close to unity in Frazer's Grove mine waters. The very lowest ratio of 17.5 was found in the 285E hopper, which (not surprisingly) is the single site with the highest recorded Zn values. The "hopper" is actually a disused vertical shaft 10 m in depth, connecting one roadway to another. This shaft is filled with broken vein material and waste rock, through which water continually drains by unsaturated flow (i.e. in the presence of O_2). It is therefore precisely the kind of site where sphalerite oxidation would be expected to occur most optimally. That Zn cannot even travel the very short distances through this shaft (10 m) without being subjected to major attenuation illustrates the rapid kinetics involved in the precipitation of mineral sinks for Zn. Even discounting the high values of the ratio associated with Zn-poor waters such as the 260 sump, the mean value of the S:Zn ratio for the Zn-rich Type II waters is 37, indicating that removal of Zn from solution is highly efficient throughout the mine.

Taking the analysis a little further, the total mine water "make" of the Frazer's Hush and Grove Rake workings combined is around 1030 $m^3.d^{-1}$, with a mean molar SO_4^{2-} concentration of 5.57×10^{-3} $moles.l^{-1}$. If all of this were derived from sphalerite oxidation, then an equimolar quantity of Zn would also be exported from the mine were transport of Zn conservative. This would amount to 375 $kg.d^{-1}$, which compares with the mean *observed* Zn loading leaving the mine of 13 $kg.d^{-1}$. In other words, only around 3.5% of the total amount of Zn which is released from sphalerite (by the same oxidation process which releases the SO_4) actually reaches the external environment. This would imply that 362 $kg.d^{-1}$ of Zn is trapped within the mined strata following sphalerite oxidation, most probably by precipitation of hydrozincite or other hydrated Zn CO_3 phases. The consumption of alkalinity which precipitation of so much Zn CO_3 would imply might in part explain why the pH and alkalinity of the Type II waters (7–7.2, and 52–100 $mg.l^{-1}$ as $CaCO_3$ respectively; Table 1) are both lower than in the Type III waters of the 260 and 270 levels (7.4–7.7, and 117–154 $mg.l^{-1}$ as $CacO_3$, respectively).

5.2. Other zinc-rich mine waters

Extreme Zn concentrations are common in acidic mine waters draining sulphidic ore bodies. For instance, the Wheal Jane mine in Cornwall, England, had as much as 1700 $mg.l^{-1}$ of Zn (and a pH of 2.6) when it first began to discharge to surface waters in 1992 (Younger, 1997a). Fuge et al. (1994) have documented mine waters flowing from the abandoned Pb–Zn mines of central Wales. In that case, the waters are acidic, and Zn concentrations can exceed 100 $mg.l^{-1}$. Beyond Britain, even higher values were reported from the Cu–Zn mines of Norway by Banks et al. (1997), with up to 5640 $mg.l^{-1}$ Zn in waters of pH 2.6 at Killingdal mine. In the nearby Løkken Cu–Zn mine they found 1100 $mg.l^{-1}$ Zn in waters of pH 4.2. The most extreme example known to the author relates to a mine at Iron Mountain, California, where negative pH values (as low as −3.6) are frequently recorded and Zn reaches 23,000 $mg.l^{-1}$ (Nordstrom and Alpers, 1999).

Clearly the Frazer's Grove mine waters, with their neutral pH and only tens of $mg.l^{-1}$ Zn are incomparably better in quality than the few examples of acidic mine waters listed above. However, they are still sufficiently Zn-rich that they cause severe ecological damage in their receiving waters, and for this reason alone they are noteworthy. Nevertheless, from a review of the international literature, it would also seem that similar Zn-rich, net alkaline mine waters have seldom (if ever) been previously described. Recent work (Nuttall and Younger, 1999) documents similar waters from nearby mines in the North Pennine Orefield, though at those sites Zn concentrations do not exceed 8 $mg.l^{-1}$. Bowell and Bruce (1995) have documented net-alkaline mine waters containing Zn which emerge from the Levant Tin Mine in Cornwall. In that case, however, the Zn originates in an acidic source within the mine which is neutralised by mixing with infiltrated sea water. Consequently, the example described by Bowell and Bruce (1995) is not an analogous occurrence of Zn-rich drainage which is of neutral pH throughout its passage through the mine (as is the case at Frazer's Grove). The paucity of published analogues for the Frazer's Grove mine waters is surprising, given the worldwide distribution of Pb–Zn orebodies similar to that of the North Pennine Orefield (cf Dunham, 1990). Undoubtedly similar mine waters must exist, but with the focus of much research being on "acid mine drainage" it may well be that net-alkaline waters carrying dissolved Zn have been overlooked in other areas.

5.3. Practical implications of geochemical results

From Fig. 3, and the foregoing discussion of the various water types in the mine, it is clear that Type II mine waters account for almost 60% of the total Zn loading leaving the mine, even though they amount to only 25% of the total pumped volume. As the bulk of the Type II waters are geographically restricted to the 285E district of the mine, this observation offers the possibility of isolating the Type II waters and treating them separately. In this way, it would be possible to achieve a dramatic improvement in the overall quality of the mine effluent whilst treating only a quarter of the total flow. By treating a small volume of waters with around 20 mg.l^{-1} Zn, rather than a large volume with 13 mg.l^{-1} Zn, the treatment processes (be they active or passive) will operate more efficiently. To expedite this plan the mining company commenced driving a 1-in-1 inclined shaft from the 295 level to intersect the 410 Level at Greencleugh Mine (Fig. 2), where a passive treatment facility could be constructed.

Equipped with a detailed knowledge of the spatial patterns of water chemistry within the mine, the mining company is also in a position (for the first time) to identify what proportion of the total flow entering the mine is from deep-seated, head-dependent sources. Identification of head-dependent inflows is an important step in conceptualizing the likely behaviour of the mine after abandonment. In particular, if it is clear that inflows will decrease as the water level in the flooding mine rises past the source strata, then both the rate of flooding and the post-flooding rate of discharge can be predictively modeled (Younger and Adams, 1999). In this particular case, the data presented in this paper served to corroborate a conceptual model which argues that almost all of the Type II and Type III sources are head-dependent, so that the only flows which will remain available for discharge to the external environment after the mine closes will be the Type I waters. Fortunately, these waters have the lowest Zn concentrations of the three types (Younger, 1998c).

6. Conclusions

1. Drainage water pumped from an active F–Pb mine in northern England has unusual chemistry: alkaline with up to 40 mg.l^{-1} Zn. Waters with Zn concentrations as high as this are usually acidic and soft, whereas these waters are circum-neutral and hard.
2. Detailed surveys of all major underground inflows to the mine revealed major, temporally persistent heterogeneities in ground water quality, with three broad types of water identified as being associated with distinct hydrostratigraphic units:
   - 2.1. Type I waters (associated with the Firestone Sill aquifer) are cool ($<10°C$), Ca–HCO$_3$–SO$_4$ waters, moderately mineralized (SEC $\leq$ 410 µS.cm^{-1}) with <4 mg.l^{-1} Zn.
   - 2.2. Type II waters (associated with the Great Limestone aquifer) are warmer ($\approx 15°C$), of Ca–SO$_4$ facies, highly mineralized (SEC $\leq$ 1500 µS.cm^{-1}) with ≤ 40 mg.l^{-1} Zn.
   - 2.3. Type III waters (in the deepest workings) are tepid ($>18°C$), of Ca–HCO$_3$–SO$_4$ facies, intermediately mineralized (SEC $\leq$ 900 µS.cm^{-1}) with ≤ 13 mg.l^{-1} Zn, and with significant Fe (≤ 12 mg.l^{-1}) and Pb (≤ 8 mg/l).
3. Monotonic increases in temperature and Cl$^-$ concentration with depth contrast with peaks in total mineralization, SO_4^{2-} and Zn at medium depth (in Type II waters). The temperature increase is ascribed to the unusually high geothermal gradient in this area (previously noted by Dunham, 1990). The peaks in total mineralization correlate with the under-drainage of recent workings of the Greencleugh Vein within the Great Limestone horizon.
4. SO$_4$, Pb and Zn are apparently sourced via oxidation of galena and sphalerite, which would release each metal in stoichiometric equality with SO$_4$. However, molal SO$_4$ concentrations typically exceed those of Pb and Zn by 2–3 orders of magnitude, which mineral equilibria suggest is due to precipitation of CO$_3$ "sinks" for these metals. The most likely "sink" for Zn is hydrozincite, which the WATEQ4F results suggest is at or near saturation in the Type II and III waters, and which has been observed actively precipitating in underground workings to the west of Frazer's Grove.
5. Contaminant loading budgets demonstrate that, although Type II waters amount to only 25% of the total ground water inflow to the mine, they account for almost 60% of the total Zn loading. This observation has important management implications for both the operational and post-abandonment phases of the mine life cycle.

Acknowledgements

The work reported here was supported by a consortium of funding sources, including the mining company (Durham Industrial Minerals Ltd (DIML)), the Environment Agency (EA) and its predecessor the National Rivers Authority and the European Commission DGXII BRITE-EURAM Programme (Contract BEST 3274). Access to the workings and safe conduct through them was kindly arranged by Jeffrey and Paul Allison (Directors), Rod Haigh and John Evans (Mine Managers) of DIML. Much assistance was also given by Stephen Brooker, Brian Whitfield, Julie Teal and Roger Inverarity of the EA, and by many colleagues at the University of Newcastle, especially Carlos Fernández Albarrán, Adam Jarvis, Charlotte Nuttall and Karen Johnson. Nick Robins of the British Geological Survey kindly arranged the δ^2H and δ^{18}O analyses.

References

Ball, J.W., Nordstrom, D.K., 1991. User's Manual for WATEQ4F, with Revised Thermodynamic Data Base and Test Cases for Calculating Speciation of Major, Trace, and Redox Elements in Natural Waters. US Geol. Surv. Open-File Report 91–183.

Banks, D., Younger, P.L., Arnesen, R.-T., Iversen, E.R., Banks, S.D., 1997. Mine-water chemistry: the good, the bad and the ugly. Environ. Geol. 32, 157–174.

Bayless, E.R., Olyphant, G.A., 1993. Acid-generating salts and their relationship to the chemistry of groundwater and storm runoff at an abandoned mine site in southwestern Indiana, USA. J. Contam. Hydrol. 12, 313–328.

Boon, M., Snijder, M., Hansfrod, G.S., Heijnen, J.J., 1998. The oxidation kinetics of zinc sulphide with *Thiobacillus ferrooxidans*. Hydrometallurgy 48, 171–186.

Bosman, D.J., 1983. Lime treatment of acid mine water and associated solids/liquid separation. Water Sci. Technol. 15, 71–84.

Bowell, R.J., Bruce, I., 1995. Geochemistry of iron ochres and mine waters from Levant Mine, Cornwall. Appl. Geochem. 10, 237–250.

Chen, M., Soulsby, C., Younger, P.L., 1997. Predicting water quality impacts from future minewater outflows in an urbanized Scottish catchment. In: Chilton, P.J., Hiscock, K.M., Younger, P.L., Morris, B., Puri, S., Nash, H., Aldous, P.J., Tellam, J., Kimblin, R., Hennings, S. (Eds.), Problems, Processes and Management, Proc. XXVII Congr. Internat. Assoc. Hydrogeol., Nottingham, UK, , 21–27 September 1997, Groundwater in the Urban Environment, vol. 1. A.A. Balkema Publishers, Rotterdam, pp. 383–388.

Dunham, K.C., 1990. Geology of the Northern Pennine Orefield, vol. I — Tyne to Stainmore. (2nd ed.). Economic Memoir of the British Geological Survey, sheets 19 and 25, and parts of 13, 24, 26, 31, 32 (England and Wales). HMSO, London.

Dvorak, D.H., Hedin, R.S., Edenborn, H.M., McIntyre, P.E., 1992. Treatment of metal-contaminated water using bacterial sulfate reduction: results from pilot-scale reactors. Biotechnol. Bioengineering 40, 609–616.

Fetter, C.W., 1999. Contaminant Hydrogeology, 2nd ed. Prentice Hall, New Jersey.

Fuge, R., Pearce, F.M., Pearce, N.J.G., Perkins, W.T., 1994. Acid-mine drainage in Wales and the influence of ochre precipitation on water chemistry. Am. Chem. Soc. Symp. Series 550, 261–274.

Gray, N.F., 1999. Water Technology. An Introduction for Environmental Scientists and Engineers. Arnold, London.

Hedin, R.S., Nairn, R.W., Kleinmann, R.L.P., 1994. Passive Treatment of Coal Mine Drainage. US Bureau Mines Inf. Circ. 9389. US Dept. Interior, Bureau of Mines, Pittsburgh, PA.

Jarvis, A.P., Younger, P.L., 1997. Dominating chemical factors in mine water induced impoverishment of the invertebrate fauna of two streams in the Durham Coalfield, UK. Chem. Ecol. 13, 249–270.

Kelly, M., 1988. Mining and the Freshwater Environment. Elsevier, London.

NRA, 1994. Abandoned Mines and the Water Environment. Report of the National Rivers Authority. Water Quality Series No 14. London, HMSO.

Nordstrom, D.K., Alpers, C.N., 1999. Negative pH, efflorescent mineralogy and consequences for environmental restoration at the Iron Mountain Superfund site, California. Proc. Nat. Acad. Sci. U.S.A. 96, 3455–3462.

Nuttall, C.A., Younger, P.L., 1999. Reconnaissance Hydrogeochemical Evaluation of an Abandoned Pb–Zn Orefield, Nent Valley, Cumbria, UK. Proc. Yorkshire Geol. Soc. 52, 395–405.

Sheppard, S.M.F., Langley, K.M., 1984. Origin of saline formation waters in northeast England: application of stable isotopes. Tras. Inst. Mining Metall. (Section B) 93, B195–B201.

Warhurst, A.C., 1999. Best available practices in mining on land of minerals. In: Nath, B., Hens, L., Compton, P., Devuyst, D. (Eds.), Environmental Management in Practice: Volume 2. Compartments, Stressors, Sectors. Routledge, London, pp. 145–165 Chapter 7.

Wilson, D., Brown, D., 1997. Fast-track provision of St Aidan's Reverse Osmosis Water-Treatment Plant. J. Chartered Inst. Water Environ. Manag. 11, 271–276.

Younger, P.L., 1995. Hydrogeochemistry of minewaters flowing from abandoned coal workings in the Durham coalfield. Quart. J. Engin. Geol. 28, S101–S113.

Younger, P.L., 1997a. The longevity of minewater pollution: a basis for decision-making. Sci. Total Environ. 194/195, 457–466.

Younger, P.L., 1997b. Minewater treatment using wetlands, Proceedings of a National Conference held 5th September 1997, Univ. Newcastle, UK. Chartered Institution of Water and Environmental Management, London.

Younger, P.L., 1998a. Coalfield abandonment: geochemical processes and hydrochemical products. In: Nicholson, K. (Ed.), Energy and the Environment. Geochemistry of Fossil, Nuclear and Renewable Resources. Soc. Environ. Geochem. Health. McGregor Science, Aberdeenshire, pp. 1–29.

Younger, P.L., 1998b. Design, construction and initial operation of full-scale compost-based passive systems for treatment of coal mine drainage and spoil leachate in the UK. In: Internat. Mine Water Association Symp. on "Mine Water and Environmental Impacts", Johannesburg, South Africa, 7–13 September 1998, vol. II, pp. 413–424.

Younger, P.L., 1998c. Environmental Implications of the Closure of Frazer's Grove Fluorspar Mine, County Durham. Report to the Environment Agency, Northumbria Area. Department of Civil Engineering, Univ. Newcastle, October 1998.

Younger, P.L., Adams, R., 1999. Predicting Mine Water Rebound. Environment Agency R & D Technical Report W179. Bristol, UK.

Younger, P.L., Harbourne, K.J., 1995. "To pump or not to pump": cost-benefit analysis of future environmental management options for the abandoned Durham Coalfield. Journal of the Chartered Institution of Water and Environmental Management 9, 405–415.

Younger, P.L., Nuttall, C.A., Jarvis, A.P., Fernández, Albarrán C.J., 1998. Novel Methods for Controlling Zinc in Mine Waters. Research Feasibility Report. Prepared for Durham Industrial Minerals Ltd under European

Commission BRITE-EURAM Contract BEST-3274. Department of Civil Engineering, Univ. Newcastle.

Younger, P.L., Pennell, R., Jarvis, A.P., Curtis, T.P., 1995. Feasibility Study to Assess the Sources and Treatment Options for Reduction of Zinc Loadings in the Rookhope Burn. NUWATER Consulting Services Ltd, Univ. Newcastle. Final Report to National Rivers Authority, Northumbria Area. November 1995.